

Comment on “Electron Correlation Effects in Resonant Inelastic X-ray Scattering of NaV_2O_5 ”

Recently, Zhang *et al.* [1] studied the resonant inelastic x-ray scattering (RIXS) of the ladder compound NaV_2O_5 . Energy losses in the RIXS were interpreted as excitations across the Hubbard gap. However, this description is based on assumptions that are not justified.

First, the Letter creates the impression that the gap in NaV_2O_5 is proportional to U . *Ab initio* calculations [2] show that the d_{xy} orbitals of a V-O-V rung form bonding and antibonding molecular orbital states as a result of $t_{\perp} \approx 0.38$ eV. These states disperse by hopping along the ladder, $t_{\parallel} \approx 0.17$ eV. Within an independent-particle framework, the ground state would be a half-filled band consisting of bonding d_{xy} molecular orbitals. Insulating behavior follows from an on-site Coulomb interaction U of 2–5 eV. Since $U \gg t_{\perp}$, a strong coupling picture is necessary. The charge-transfer gap is then not proportional to U but to $2t_{\perp} - J_{\perp}$, where $J_{\perp} \approx 4t_{\perp}^2/U$.

Second, RIXS at the L edge in transition metal compounds is not well suited to study charge-transfer excitations. The strong core hole potential leads to the formation of an exciton of the core hole and the excited electron. This effect is ignored by Zhang *et al.*, who claim that the excited electron is delocalized in an upper Hubbard band. This should be contrasted with excitations at the K edge. Here the core hole is not well screened by the $4p$ electron and excitations across the gap are necessary to screen the core hole.

Third, the polarization condition used in the experiment does not allow the observation of the lowest excited state of NaV_2O_5 . Figures 1(b) and 1(c) show the RIXS spectra for the absorption energies, indicated by labels a–f in Fig. 1(a), for two different polarization conditions (see insets). Calculations were done for a four-site Hubbard model of d_{xy} orbitals. On the site where the RIXS process takes place, all the $2p$ and $3d$ orbitals, the spin-orbit coupling, and the full dd and pd multiplet interaction are included. The RIXS spectra of Zhang *et al.* [1] were measured in a very particular polarization condition with the incoming polarization π in the scattering plane and a 90° angle between the incoming and scattered radiation. For the outgoing x rays, both parallel (π) and perpendicular (σ) polarization components are present. This geometry is often used to remove the elastic peak from the RIXS spectra. Since the total scattering operator does not include the totally symmetric term, a $d_{xy} \rightarrow d_{xy}$ transition becomes forbidden. However, not only the elastic peak is affected. This becomes clear when comparing the calculations for RIXS in Figs. 1(b) and 1(c). Note that at the incoming energy indicated by c, we see features A and B for $\sigma \rightarrow \pi\sigma$ and only feature B for $\pi \rightarrow \pi\sigma$. Feature A is an on-rung transition between bonding and antibonding d_{xy} molecular orbitals, which becomes forbidden in a 90°

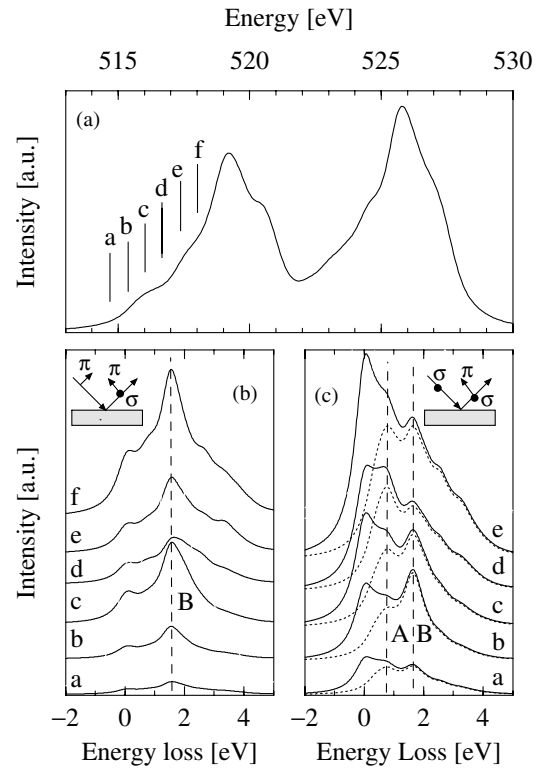


FIG. 1. (a) The solid line shows the x-ray absorption spectrum for a four-site cluster. The letters a–f indicate the various incident energies. RIXS data on an energy-loss scale $\hbar(\omega - \omega')$ in the $\pi \rightarrow \pi\sigma$ and $\sigma \rightarrow \pi\sigma$ configurations are shown in (b) and (c), respectively. Also shown in (c) are the RIXS spectra with the elastic contribution removed (dotted line).

$\pi \rightarrow \pi\sigma$ geometry. The smaller excitation energy of 0.8 eV is in agreement with that found in optical spectroscopy [3]. The energy loss feature at 1.5 eV observed in the geometry used by Zhang *et al.* (indicated by B) corresponds to a local $d_{xy} \rightarrow d_{yz,zx}$ transition.

M.v.V. is supported by the Department of Energy (DE-FG02-03ER46097) and the U.S. Department of Education.

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Received 2 June 2003; published 26 May 2004

DOI: 10.1103/PhysRevLett.92.219701

PACS numbers: 78.70.En, 71.20.Be, 78.70.Ck

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